Atty. Dkt. No. 023312-0109

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Takashi NAGASE et. al.

Title: METHOD OF MANUFACTURING NANO-GAP ELECTRODE

Appl. No.: 10/662,886

Filing Date: 09/16/2003

Examiner: Ahmed, Shamim

Art Unit: 1765

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

1. I am a co-inventor of the captioned application, US Application No. 10/662,886.

2. My educational background is in Physics and Electronics and I have worked as a researcher at the National Institute of Communication Technology, as shown in my CV attached hereto as Exhibit 1.

3. I have reviewed the specifications of U.S. Patent No. 6,245,249, hereinafter called Yamada and U.S. Patent Application Publication No. US 2003/0067259, hereinafter called Nishimura, and understood them. I have also reviewed and understand the Office Action dated June 10, 2005 of the captioned application.

4. As the Examiner pointed out in the outstanding Office Action, Nishimura fails to disclose that the metal mask is etched by a focused ion beam, the use of which is one of the features of the present invention. Without focused ion beam, I believe that it would be very difficult to produce an electrode with a nano-scale gap.

5. There is no teaching in Yamada of producing an electrode with a nano-scale gap, even though Yamada discloses the use of a focused ion beam. The target of Yamada is different and larger than our target, thus one of ordinary skill in the art could not have produced or would not have been motivated to produce an electrode with a nano-scale gap by using the focused ion beam disclosed in Yamada.

6. I do not believe that one of ordinary skill in the art, at the time of the invention, would have realized that it was possible to produce an electrode with nano-scale gap in accordance with the claims of the present application.

7. The difficulties of producing an electrode with nano-scale gap in accordance with the claims of the present application are discussed in (1) the peer reviewed article published as T. Nagase, T. Kubota and S. Mashiko, "Fabrication of nano-gap electrodes for measuring electrical properties of organic molecules using a focused ion beam", Thin Solid Films, Vol. 438-439, pp. 374-377 (2003), attached hereto as Exhibit 2, and (2) Paragraph Nos. [0004] to [0007] of the specification of the captioned application.

8. For these reasons, it is my belief that one of ordinary skill in the art could not have practiced the claimed invention based on the teachings of Yamada and Nishimura.

9. I hereby declare that all the statements made herein of my known knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements are so made punishable by fine or imprisonment, or both, under Section 101 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

December 5, 2005
Date

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EXHIBIT 1

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- Amorphous Semiconductor Physics
- Polymeric Semiconductor Physics

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Publications:

1. T. Nagase, K. Gamo, T. Kubota and S. Mashiko, "Direct fabrication of nano-gap electrodes by focused ion beam etching"; *Thin Solid Films* (2005) in press.
2. M. Ando, H. Naito, T. Nagase and Y. Kanemitsu, "Transient photocurrent of (silicon nanocrystals)-(organic polysilane) composite", *Thin Solid Films* (2005) in press.
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4. T. Nagase, K. Gamo, T. Kubota and S. Mashiko, "Maskless fabrication of nanoelectrode structures with nanogaps by using Ga focused ion beams", *Microelectronic Engineering*, Vol. **78-79**, pp. 253-259 (2005).
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6. H. Naito and T. Nagase, "A method for measuring localized-state distributions from transient photoconductivity in amorphous and polymeric semiconductors", in *Recent Research Developments in Non-Crystalline Solids*, Vol. **2**, pp. 425-444 (2002) (Transworld Research Network, Trivandrum).
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EXHIBIT 2

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Fabrication of nano-gap electrodes for measuring electrical properties of organic molecules using a focused ion beam

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Abstract

Molecular electronics, in which a single molecule is used as an element, requires the ability to interface nanometer-sized molecules to macroscopic electronic circuits. For this end, a simple and highly reproducible method to fabricate metallic electrodes with nanometer gaps is proposed. This method consists of the patterning of a metallic mask by focused ion beam (FIB) etching and the pattern transfer to an underlying metallic electrode by dry etching. Metallic electrodes with gaps of 5–8 nm, which are much smaller than the minimum diameter of a FIB, can be reproducibly fabricated using this method. Electrical measurements of the electrodes reveal very good insulating characteristics. These electrodes are expected to be useful for electrically measuring single molecules.

Keywords: Molecular electronics; Focused ion beam; Nano-gap electrode

1. Introduction

Recently, molecular electronic devices [1], i.e. electronic devices with single molecules as the active elements have received considerable attention, as possible candidates miniaturize future electronic devices. This is because Si-based microelectronics is expected to reach its miniaturization limits in the next 10 years and because molecular electronic devices conceptually provide important technological advantages both for size reduction to the nanometer scale and for enhanced functionality. For example, since modern chemistry can synthesize a large variety of perfectly defined single molecules, one may expect that molecules with the desired electrical functions can be produced. For realization of molecular electronics, the investigation of the electrical properties of individual molecules is of fundamental importance. The electrical characterization of single molecules requires the fabrication of pairs of metallic electrodes, the gaps of which are comparable in size to single molecules, i.e. nanometer size (henceforth, referred to as 'nano-gap electrodes'). However, fabricating such electrodes presents difficulty because single molecules are much smaller than the resolution limits (approx. 20 nm) of conventional electron beam (EB) lithography.

A number of methods for fabricating nano-gap electrodes has already been demonstrated [2–8]. In particular, the mechanical break junction [4], electrochemical deposition [5–7] and electromigration methods [8] have generally been used for fabricating nano-gap electrodes. These methods allow the fabrication of nano-gap electrodes with a gap of few nanometers, however, involve complicated processes that are not easy to control and have low yields. Focused ion beam (FIB) lithography has also been used to fabricate nanostructures. Because the minimum diameter of a FIB is relatively small (approx. 5–20 nm) and the proximity effects of FIB lithography are much less than that of EB lithography, FIB lithography can produce smaller structures than EB lithography. In fact, a resist groove with a width of 8–10 nm was produced using FIB exposure [9]. However, applying FIB lithography to the fabrication of nano-gap electrodes incurs two major problems. First, FIB exposure may cause a change in the insulating characteristic of a nano-gap electrode because highly accelerated ions can easily reach the insulating substrate in the inter-electrode region across an organic resist film and a thin metallic electrode. Second, a thin resist film is required for fabricating narrow gaps in order to reduce the resist's exposure by scattered ions in the resist film [9]. These

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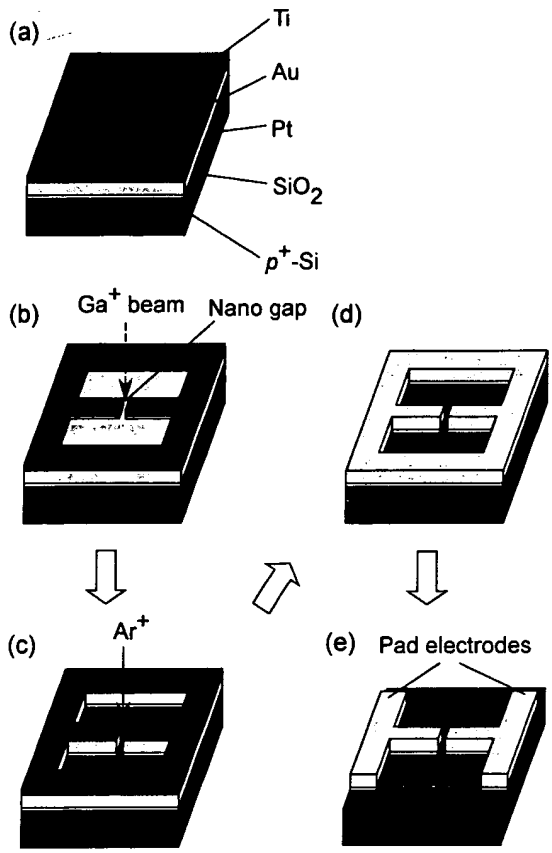

Fig. 1. Schematic diagram of the FIB lithographic process for fabricating nano-gap electrodes: (a) Structure of the sample. (b) Mask fabrication by FIB etching. (c) Pattern transfer by Ar^+ etching. (d) Mask removal by wet etching. (e) Pad electrodes fabrication by photolithography.

problems are related. For example, the use of a metallic electrode that is thicker than the range of a ion beam seems to be an invalid means to overcome the first problem because such a thick metallic electrode cannot be transferred using dry etching with the thin resist film, required because of the second problem.

In this article, we propose a simple and highly reproducible method for fabricating nano-gap electrodes using a FIB.

2. Experiments

This method is based on patterning a mask by FIB etching and transferring the pattern to an underlying electrode by dry etching. Thin and thick metallic films are used as the mask and the electrode, respectively; this overcomes the two problems mentioned above.

The structure of the sample we used is illustrated in Fig. 1a. The substrate was a highly doped p type Si (p^+-Si) wafer with a ~300-nm-thick film of thermally grown SiO_2. A triple-layered metallic film, consisting of ~12-nm-thick Pt, ~70-nm-thick Au and ~44-nm-thick Ti, was deposited by sputtering on the substrate. The Au and Ti films were used as an electrode and a mask, respectively. The Pt film was used to promote the adhesion of Au to the underlying SiO_2 surface. We used this Ti/Au/Pt/SiO_2/p^+-Si structure as an original sample for our method.

The lithographic process for fabricating nano-gap electrodes is schematically shown in Fig. 1b–e. First, a Ti mask was patterned by FIB etching (Fig. 1b). FIB etching was performed using a FIB system equipped with a 30-keV Ga^+ source (Seiko Instruments JFIB-2300). The minimum beam diameter in the system was ~12 nm (full width at half maximum). To reduce the FIB processing time, the fabrication of large patterns was performed using a relatively broad beam (approx. 22 nm in diameter) and the narrow beam (approx. 12 nm) was only employed to fabricate nano-gap patterns. The exposure dose of 10^{17}–10^{18} ions/cm^2 was used. To completely remove the residual Ti left on the Au surface in the FIB etched regions, the underlying Au was etched to a depth of 20–30 nm from the surface. Because the penetration depth of a 30-keV Ga^+ into the Au and Pt is ~30 nm, the Ga^+ can be stopped in the Au/Pt electrodes. Hence, there was no ion implantation in the SiO_2 substrate.

Next, the Ti mask pattern was transferred to the underlying Au/Pt electrode by Ar^+ etching (Fig. 1c). To obtain steep sidewalls, we used an anisotropic ion etcher (Elionix EIS-200ER). Accelerated (1 keV) Ar ions were exposed to the Au/Pt electrode through the Ti mask with respect to the substrate normal. This etch has a selectivity better than 5:1 of Au or Pt to Ti. In order, to completely remove the residual Pt left on the SiO_2 substrate in unmasked regions, the underlying SiO_2 substrate was slightly under etched (approx. 3–10 nm).

Finally, the Ti mask was removed by etching in hot H_2SO_4:H_2O_2 (3:1) solution (approx. 60–70 °C) (Fig. 1d). This hot acid solution had a chemical selectivity, and so could remove only the Ti without damaging the Au/Pt electrode.

For electrical measurements, the fabricated nano-gap electrode was connected to pad electrodes using photolithography (Fig. 1e). To completely eliminate organic contaminations on the sample, it was immersed in hot H_2SO_4:H_2O_2 (3:1) solution, rinsed thoroughly with de-ionized water, washed ultrasonically with acetone and de-ionized water, and finally cleaned with an O_2 plasma and an ozone cleaner.

We investigated the insulating characteristics of the fabricated nano-gap electrodes. The electrical properties of the nano-gap electrodes were measured with a standard two terminal technique using an electrometer (Keithley 6517A) and a DC source (Advantest TR6143) at room temperature in vacuum. The observation of the nano-gap electrodes was carried out using a field-

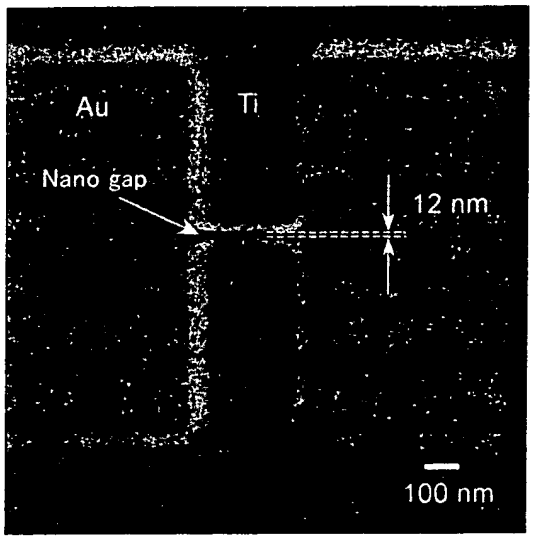

Fig. 2. Scanning ion microscope image of nano-gap electrode pattern after FIB etching. Image size is 1.5×1.5 μm^2.

emission Scanning electron microscope (SEM) (Jeol JSM-6700F) and a contact-mode Atomic force microscope (AFM) (Digital Instruments Nanoscope IIIa) with a Si_3N_4 tip. To prevent contaminations, the electrical measurements were performed before the SEM and AFM observations.

3. Results and discussion

Fig. 2 shows a scanning ion microscope image of the mask pattern of a nano-gap electrode after FIB etching. The observation was performed using the FIB system at 1.5×1.5 μm^2, in which a part of the entire fabricated nano-gap electrode pattern was imaged. The two rectangles and the single line were etched using a relatively broad beam and a narrow beam, respectively. The single line corresponds to a nano-gap pattern. The border of the nano-gap electrode pattern is slightly damaged, as seen in the figure. This damage is most likely caused by etching at the Ti surface with ions in the FIB tail because the FIB has a Gaussian intensity profile and slight etching occurs even with a relatively weak FIB in the tail. The figure shows that the width of the etched gap is almost the same as the minimum beam diameter (approx. 12 nm). Thus, we found that the FIB etching of metallic films could produce narrow gaps of the same size as the minimum beam diameter.

Fig. 3 shows a SEM image of the fabricated nano-gap electrode on the SiO_2 substrate after transferring the Ti mask pattern by Ar^+ etching and etching the Ti mask with the hot acid solution. It is seen in the figure that the Au of both sides of the nano gap is slightly etched. These regions correspond to the damaged Ti regions. We measured the reduced thickness of the Au of both side of the nano gap using AFM. The reduced thickness

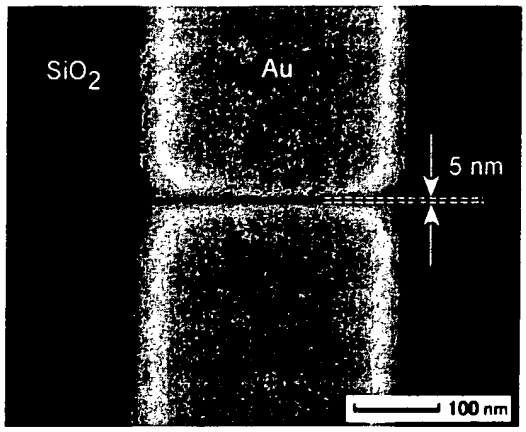

Fig. 3. SEM image of nano-gap electrode on SiO_2 substrate after transferring Ti mask pattern by Ar^+ etching and etching Ti mask with hot acid solution. Width of gap is ~5 nm.

of the Au was less than 10 nm (not shown). These results indicate that the damaged Ti remains until just before Ar^+ etching is finished and that the Ti mask works adequately as an etching mask. It can be clearly seen in the figure that the gap width is ~5 nm, which is much smaller than the minimum beam diameter (approx. 12 nm). It was found that most of fabricated nano-gap electrodes had gaps smaller than minimum beam diameter. We consider that ion etching with the top of a FIB forms such narrow gaps because the FIB has a Gaussian intensity profile and the top of the FIB has the highest etch rate. We found that the gaps of 5–8 nm could be reproducibly fabricated using our method.

Fig. 4 shows a typical current–voltage characteristic of a nano-gap electrode measured at 296 K in vacuum. The current is of the order of fA, which is roughly the resolution limit of our instrument. Similar order current was observed for most of the nano-gap electrodes fabricated using this method. These results indicate that

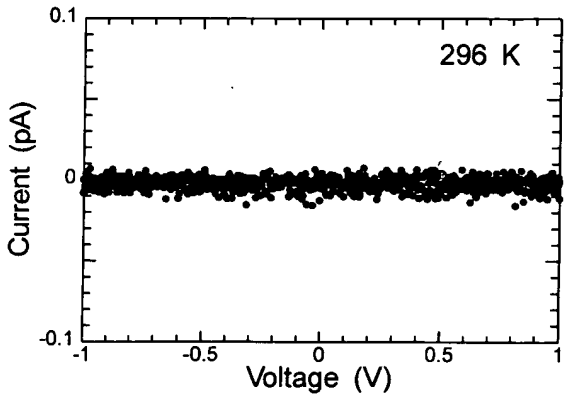

Fig. 4. Typical current–voltage characteristic of nano-gap electrode measured at 296 K in vacuum.

the nano-gap electrodes fabricated using this method have very good insulating characteristics.

4. Conclusion

We proposed a simple and highly reproducible method for fabricating metallic electrodes with nanometer gaps using a focused ion beam (FIB). This method is based on the patterning of a metallic mask by FIB etching and the lithographic transfer of the pattern to underlying a metallic electrode. Using this method, Au/Pt electrodes with gaps of 5–8 nm were reproducibly fabricated on SiO_2 substrates. These gaps were smaller than the minimum diameter of the FIB (approx. 12 nm). The electrical measurements of the electrodes revealed very good insulating characteristics. We believe that these electrodes are practical for electrically measuring single molecules.

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